



# Electrical Properties of Acceptor-Doped BaCeO<sub>3</sub>

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## Abstract

Barium cerate exhibits high protonic conductivity in gas atmospheres containing water vapour, especially when modified with a trivalent dopant such as Y, Gd, Yb, Nd, Sm or Dy. Such materials can be used as solid electrolytes in intermediate temperature solid oxide fuel cells. In the present work, the influence of Y and Gd dopants on the electrical properties of BaCeO<sub>3</sub> was investigated using the Electrochemical Impedance Spectroscopy (EIS) technique. Oxygen nonstoichiometry and valence of cerium were studied with the analytical iodometric method. Samples were prepared in solid-state reactions. It was found that the electrical properties depend on the preparation method. Doping with an acceptor, in this case Y or Gd, leads to substantial changes to both bulk and grain boundary electrical conductivity in comparison with undoped materials.

**Keywords:** Barium cerate, Electrical properties, Impedance spectroscopy, Nonstoichiometry

## WŁAŚCIWOŚCI ELEKTRYCZNE BaCeO<sub>3</sub> DOMIESZKOWANEGO AKCEPTOROWO

Cerany baru wykazują wysokie przewodnictwo protonowe w atmosferach gazowych zawierających parę wodną szczególnie wtedy, gdy zostały zmodyfikowane trójwartościowymi domieszkami Y, Gd, Yb, Nd, Sm lub Dy. Takie materiały mogą być wykorzystywane jako elektrolity stałe w komórkach paliwowych stałotlenkowych do pracy w temperaturach pośrednich. W prezentowanej pracy zbadano wpływ domieszek Y i Gd na właściwości elektryczne BaCeO<sub>3</sub> przy wykorzystaniu elektrochemicznej spektroskopii impedancyjnej (EIS). Za pomocą analitycznej metody miareczkowania jodometrycznego oznaczono niestechiometrię tlenową i wartościowość ceru. Próbkę przygotowano wykorzystując reakcje zachodzące w stanie stałym. Stwierdzono, że właściwości elektryczne zależą od metody preparatyki. Domieszkowanie akceptorem, w tym przypadku Y lub Gd, prowadzi do znacznych zmian przewodnictwa elektrycznego, zarówno objętościowego jak i po granicach, w porównaniu z materiałami niedomieszkowanymi.

**Słowa kluczowe:** ceran baru, właściwości elektryczne, spektroskopia impedancyjna, niestechiometria

## 1. Introduction

Solid oxide fuel cells, SOFC's, attract high interest because of their high energy conversion efficiency and thus low environmental impact. Traditional high-temperature fuel cells are based on yttria-stabilized zirconia (YSZ) electrolyte which requires operation at a temperature above 1100 K to minimize the high ohmic loss due to the low ionic conductivity of the electrolyte [1]. However, such a high operation temperature causes many problems mainly for sealing and interconnectors, reactions between connected cell components, thermal expansion mismatch, long startup and shutdown times required to avoid thermal shocks. Therefore, great efforts have been made to develop a new type of intermediate temperature solid oxide fuel cells, IT-SOFCs. Lowering the operating temperature to 870-1070 K reduces the abovementioned drawbacks. In particular, it allows low-cost metallic materials, to be used, such as stain-less steels for the interconnection and construction materials which improves the cell performance as well as lowers fabrication costs [2]. Recently, a metal-supported SOFC, an alternative

to conventional electrolyte or electrode-supported SOFCs, has been developed [3]. A crucial issue in the development of IT-SOFCs is the choice of a highly ion-conductive solid electrolyte, capable of operating at intermediate temperatures.

High-temperature proton-conducting oxide perovskites, especially the acceptor-doped BaCeO<sub>3</sub>, promise solid electrolytes for the IT-SOFCs, because of their high protonic conductivity and low activation energy [4-6]. Iwahara *et al.* [7, 8] first tried to fabricate fuel cells with BaCeO<sub>3</sub>-based solid electrolyte and porous platinum electrodes. They observed an increase in the current density with temperature within 1073-1273 K. However, as the temperature was raised, the predominant charge carrier in the electrolyte changed from proton to oxygen ion. The use of the protonic electrolyte instead of an oxygen ion conductor has distinctive features on cell maintenance. Fuel circulation is unnecessary in the case of a protonic electrolyte cell because no water is generated in the fuel electrolyte. An interesting proposition has been made by Shimura *et al.* [9] who used two layered electrolytes composed of ionic conductor (YSZ) and a protonic conductor. Protonic conductors have not been yet commercialized

as the solid electrolyte in fuel cells because of low stability under operating conditions, e.g. in humid or CO<sub>2</sub>-containing atmosphere. There were several attempts to improve chemical stability of BaCeO<sub>3</sub>-based materials. Ma *et al.* [10] studied the ionic conductivity of Ba<sub>x</sub>Ce<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> for  $x > 1$ ;  $x = 0$  and  $x < 1$ . They claimed that the specimen with  $x = 0.95$  has not only the highest conductivity, but also the highest chemical stability. On the other hand, Pasierb *et al.* [11] discovered that titanium doping of barium cerate improved its resistance against CO<sub>2</sub> corrosion. Also, an appropriate choice of the acceptor-type dopant may improve the chemical stability. According to Taniguchi *et al.* [12], the fuel cell with gadolinium-doped barium cerate used as the electrolyte exhibited good performance and long life at 1073 K.

The aim of the present paper was the preparation and determination of structural and electrical properties of acceptor-doped barium cerate. The acceptor centers were formed in controlled process either by doping them with trivalent ions (Y<sup>3+</sup> or Gd<sup>3+</sup>) or by changing the A/B ratio in the BaCeO<sub>3</sub> perovskite structure.

## 2. Experimental

### 2.1. Preparation of samples

(Ba<sub>1-y</sub>Sr<sub>y</sub>)<sub>z</sub>Ce<sub>1-x</sub>M<sub>x</sub>O<sub>3</sub> ( $x = 0$  or  $0.1$ ,  $y = 0$  or  $0.1$ ,  $z = 1$  or  $0.9$ ) powders were prepared by the solid-state reaction method. Appropriate amounts (corresponding to predicted final materials compositions of barium carbonate BaCO<sub>3</sub>, SrCO<sub>3</sub>, cerium(IV) oxide CeO<sub>2</sub> (Aldrich Chemical Company 99.9 %, Germany) and either yttrium or gadolinium nitrate M(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O; M = Y or Gd) solution were mixed. Mixtures were dried at 80°C, pressed and then sintered at 1200°C for 24 h. Powders were placed in a pellet die ( $\phi = 25$  mm) at 25 MPa, isostatically pressed at 250 MPa and sintered at 1500°C for 24 h in air atmosphere.

### 2.2. XRD analysis

X-ray diffraction, XRD, measurements were performed on X'Pert MPD Philips diffractometer using CuK<sub>α</sub> filtered radiation within the 2θ range of 10-90°.

### 2.3. EIS measurements

The electrochemical impedance spectroscopy, EIS, was done using the Solartron FRA 1260 coupled with Solartron 1296 Dielectric Interface. The amplitude of the sinusoidal voltage was 20 mV. The impedance spectra were recorded in the frequency range of 0.1 Hz – 1 MHz and p(O<sub>2</sub>) of 10<sup>-15</sup>–10<sup>4</sup> Pa.

### 2.4. Determination of oxygen nonstoichiometry

The oxygen nonstoichiometry, δ, in the samples was determined with the Bunsen-Rupp method. The method consists of treating a sample with concentrated HCl, which leads to the reduction of the Ce<sup>4+</sup> ions to Ce<sup>3+</sup>, and determination of the evolved chlorine by iodometric titration.

## 3. Results and discussion

XRD patterns of BaCeO<sub>3</sub>, BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3</sub>, Ba<sub>0.9</sub>Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3</sub> and Ba<sub>0.9</sub>Sr<sub>0.1</sub>Ce<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3</sub> are shown in Figs. 1a – 1d, respectively. The diffraction patterns are typical for highly crystalline materials. A detailed analysis revealed that they crystallized in orthorhombic Pmcn perovskite structure. No additional phases were found except of Ba<sub>0.9</sub>Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3</sub>. The obtained results are in general agreement with the results presented in [10] where the solubility limit of yttrium in barium cerate was determined as 20 mol%. On the other hand, Fig. 1c indicates that solubility of gadolinium was surpassed.

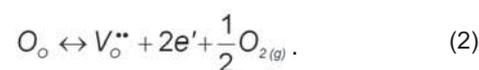
A detailed analysis of the additional reflexes in Fig. 1c revealed that they come from the fluorite phase of CeO<sub>2</sub> (probably gadolinium doped).

Figs. 2 and 3 show typical impedance spectra at 573 K for BaCeO<sub>3</sub> and Ba<sub>0.9</sub>(Ce<sub>0.9</sub>Gd<sub>0.1</sub>)O<sub>3-δ</sub>, respectively in dry and wet air atmospheres. The results are plotted on the complex impedance plane: -Z'' versus Z' (where Z'' and Z' describe imaginary and real parts of impedance, respectively). Two or three semicircular parts may be distinguished. It is commonly accepted that the high-frequency semicircle corresponds to the bulk. The second semicircle is related to a partial blocking of mobile ions at the internal surfaces such as grain boundaries and other structural defects like pores and cracks. The third, if present, characterizes electrode reactions. The impedance data were analyzed in terms of equivalent circuit [13]. Fig. 4 illustrates the equivalent circuit used to determine electrical properties of the studied materials. CPE denotes constant phase element whose impedance was given by

$$Z_{CPE} = \frac{1}{A \cdot (j \cdot \omega)^n}, \quad (1)$$

where:  $A$  and  $n$  are fit parameters independent of frequency,  $j$  is an imaginary unit and  $\omega$  is an angular frequency. The determined parameters of the equivalent circuit for both BaCeO<sub>3-δ</sub> and Ba<sub>0.9</sub>(Ce<sub>0.9</sub>Gd<sub>0.1</sub>)O<sub>3-δ</sub> are collected in Table 1.

No significant effect of bulk electrical conductivity in dry and wet air was observed. The presence of water in gas atmosphere leads to the decrease of grain boundary resistivity by ca. 27 %. The electrical properties of undoped BaCeO<sub>3</sub> can be explained in terms of interaction of the solid with gas atmosphere and the resulting oxygen nonstoichiometry [14]:



Undoped BaCeO<sub>3</sub> exhibits only low electrical conductivity. Its electrical properties may be changed drastically by the formation of acceptor-type point defects. The negative charge (in respect to lattice) is then compensated for by positive oxygen vacancies V<sub>o</sub><sup>\*\*</sup>.

Such a material exposed in hydrogen-containing gas atmosphere exhibits protonic conductivity [7-9]. Contrary to the case of undoped BaCeO<sub>3</sub> sample, the impedance spectrum of Ba<sub>0.9</sub>(Ce<sub>0.9</sub>Gd<sub>0.1</sub>)O<sub>3-δ</sub> is more complex (Fig. 3). It may be due observed heterogeneity of this sample (Fig. 1c). Nevertheless, three semicircles can be identified.

The formation of Ba-deficit sample: Ba<sub>1-z</sub>CeO<sub>3-δ</sub> can be expressed by the following reaction:

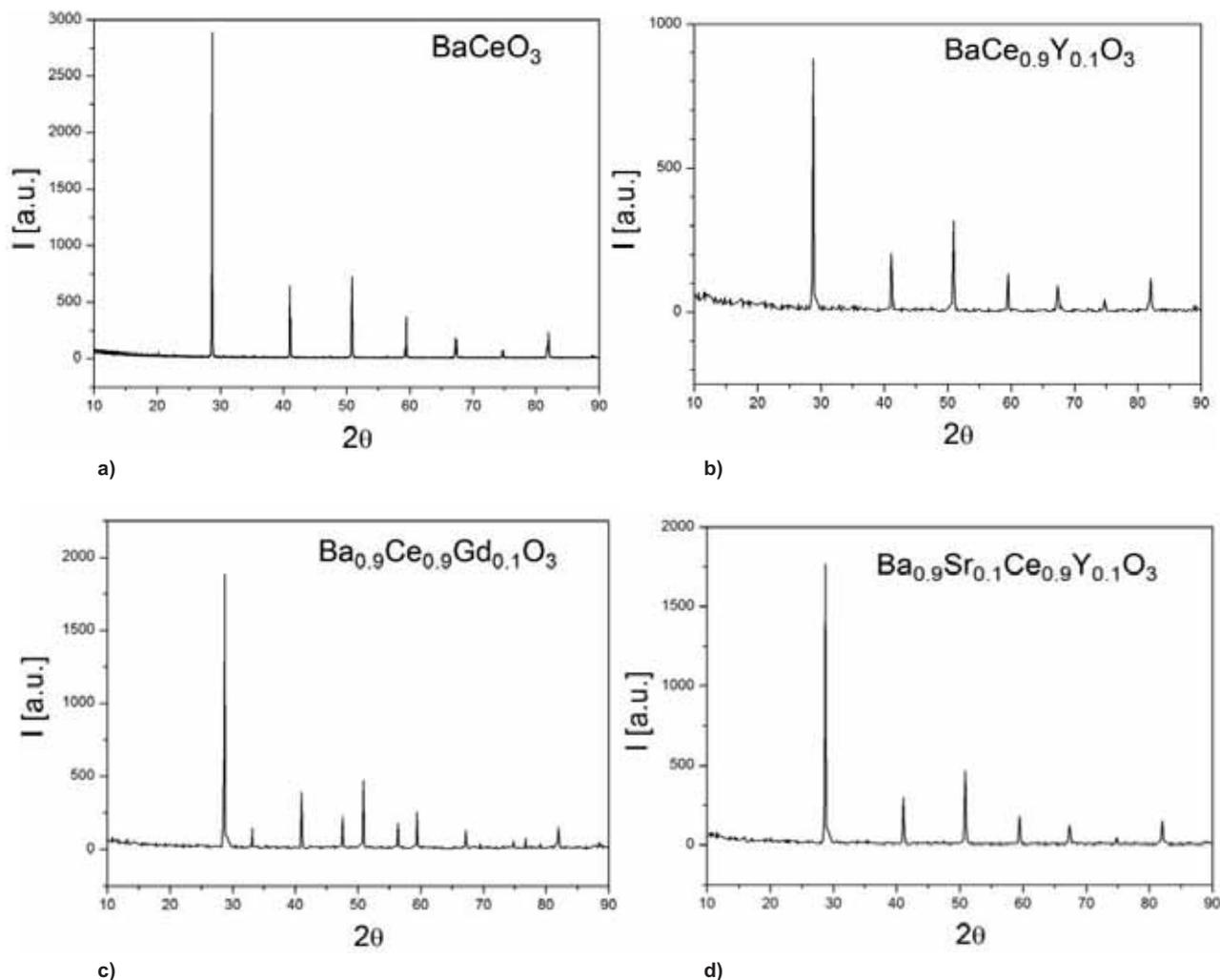
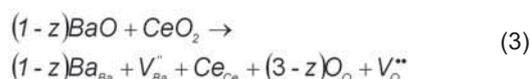
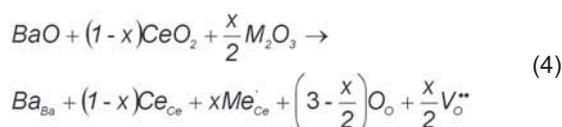


Fig. 1. XRD patterns: a) BaCeO<sub>3</sub>, b) BaCe<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3</sub>, c) BaCe<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3</sub> and d) Ba<sub>0.9</sub>Sr<sub>0.1</sub>Ce<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3</sub>.



On the other hand, the incorporation of M<sub>2</sub>O<sub>3</sub> rare earth oxide (e.g. M = Y or Gd) is described by the reaction:



Oxygen vacancies formed according to reactions (2)-(4) are the source of mobile oxygen ions in perovskite lattice. As it results from Eq. (2), undoped material exhibits mixed electronic-ionic conductivity. The total conductivity is rather low due to low departure from stoichiometry. As it results from Eqs. (3) and (4), deficit of barium ( $z > 0$ ) as well as doping by trivalent ions M<sup>3+</sup> ( $x > 0$ ) lead to the increase of oxygen vacancies and related oxygen ion conductivity in dry atmospheres. In the presence of water vapour the creation of protonic defects occurs according to the following reaction:

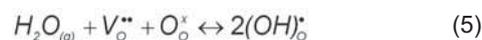


Table 1. Parameters of the equivalent circuit for BaCeO<sub>3-δ</sub> and Ba<sub>0.9</sub>(Ce<sub>0.9</sub>Gd<sub>0.1</sub>)O<sub>3-δ</sub>.

Parameter	Sample			
	BaCeO <sub>3-δ</sub>		Ba <sub>0.9</sub> (Ce <sub>0.9</sub> Gd <sub>0.1</sub> )O <sub>3-δ</sub>	
	dry	wet	dry	wet
R <sub>1</sub> [kΩ]	101 (± 3.8%)	107 (± 3.8%)	1.98 (± 1.3%)	11.96 (± 1.3%)
n <sub>1</sub>	0.81 (± 3.8%)	0.75 (± 2.2%)	-	-
A <sub>1</sub> ·10 <sup>10</sup> [Ω·s <sup>-n1</sup> ]	1.6 (± 22%)	3.7 (± 23%)	-	-
R <sub>2</sub> [kΩ]	344 (± 0.57%)	250 (± 0.61%)	250 (± 0.61%)	112.6 (± 0.8%)
n <sub>2</sub>	0.82 (± 0.53%)	0.80 (± 0.58%)	0.80 (± 0.58%)	0.65 (± 0.6%)
A <sub>2</sub> ·10 <sup>10</sup> [Ω·s <sup>-n2</sup> ]	17.7 (± 3.7%)	19.6 (± 3.9%)	19.6 (± 3.9%)	1640 (± 4.1%)
R <sub>3</sub> [kΩ]	-	-	9.9 (± 1.4%)	14.8 (± 4%)
n <sub>3</sub>	-	-	0.43 (± 1.4%)	0.46 (± 4%)
A <sub>3</sub> ·10 <sup>6</sup> [Ω·s <sup>-n3</sup> ]	-	-	3.8 (± 3.3%)	2.4 (± 6%)

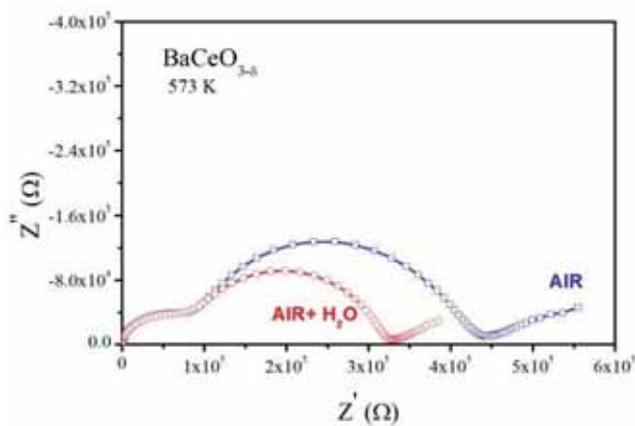


Fig. 2. EIS spectra of undoped BaCeO<sub>3</sub> at 573 K in dry and wet air atmosphere.

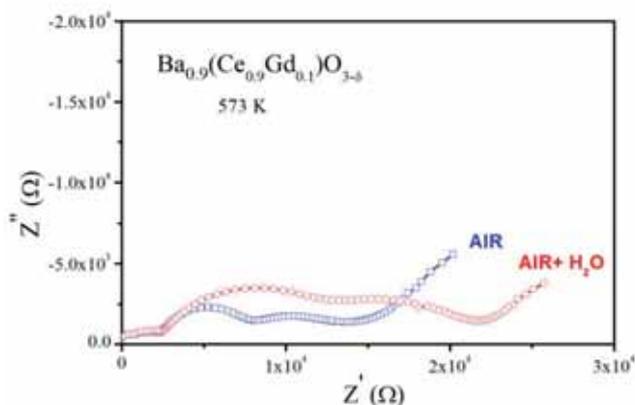


Fig. 3. EIS spectra of Ba<sub>0.9</sub>Ce<sub>0.9</sub>Gd<sub>0.1</sub>O<sub>3-d</sub> at 573 K in dry and air atmosphere.

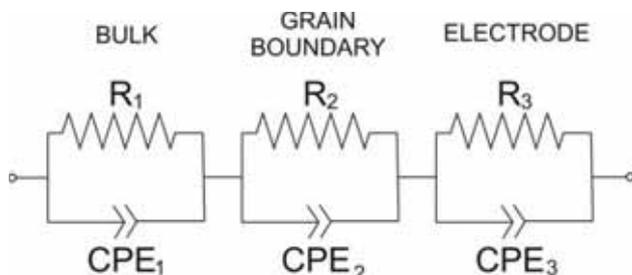


Fig. 4. Equivalent circuit.

According to the equations (3)-(5), both barium deficit and M<sub>2</sub>O<sub>3</sub> incorporation may be applied as controlled formation of protonic defects and related protonic conductivity in barium cerate.

Fig. 5 illustrates the departure from stoichiometric composition,  $\delta$ , in oxygen sub-lattice determined from analytical Bunsen-Rupp method. Oxygen nonstoichiometry,  $\delta$ , of the undoped sample is about 10<sup>-3</sup>, and it is over one order of magnitude higher for acceptor-doped materials.

Assuming that:

- 1) all element components have nominal valence (i.e. +2, +4, +3, -2 for Ba, Ce, M and O, respectively),
- 2) concentration of oxygen vacancies formed in reaction of interaction solid-gas (Eq. 1) is negligible,
- 3) concentration of electronic defects (electrons and electron holes) is negligible,

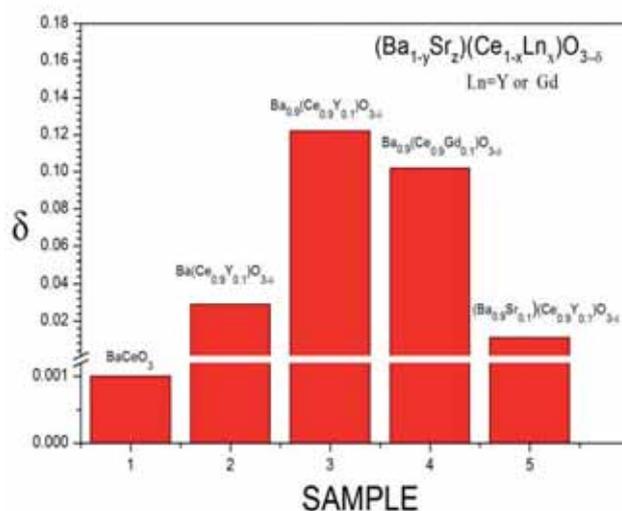


Fig. 5. Oxygen nonstoichiometry,  $\delta$ , of the undoped and acceptor doped barium cerate.

- 4) dopant elements, M, incorporated substitutionally into cerium sublattice only,
- 5) the following formula is valid:

$$\delta = z + \frac{x}{2} = A, \quad (6)$$

where A is called the nominal concentration of acceptors. A straight line in Fig. 7 illustrates the dependence (5). Undoped barium cerate shows oxygen nonstoichiometry  $\delta \approx 1 \cdot 10^{-3}$ . This value results from the reaction (2). On the other hand, nonstoichiometry,  $\delta$ , of doped samples is much higher and observed departure of the experimental points from the theoretical straight line dependence may be explained by either partial reduction of cerium ions, Ce<sup>4+</sup> to Ce<sup>3+</sup> [15] or a part of M ions occupied simultaneously barium sublattice, forming donor-type canters M<sup>•</sup><sub>Ba</sub> [16].

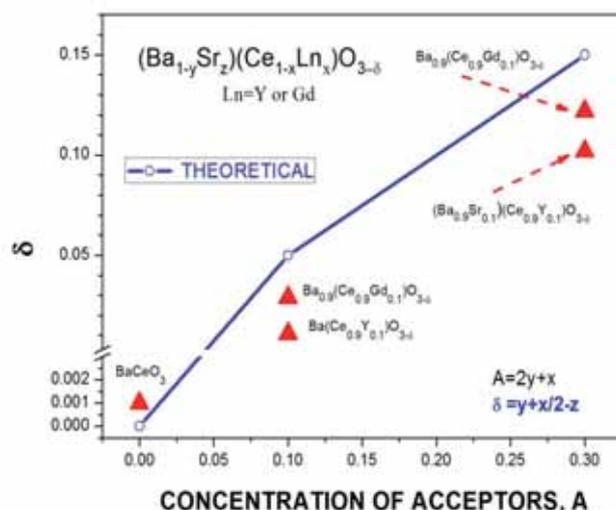


Fig. 6. Dependence of  $\delta$  on nominal concentration of acceptors.

#### 4. Conclusions

The samples of the composition: (Ba<sub>1-y</sub>Sr<sub>z</sub>)Ce<sub>1-x</sub>M<sub>x</sub>O<sub>3</sub> (x = 0 or 0.1, y = 0 or 0.1, z = 1 or 0.9) were prepared by the solid state reaction. The samples exhibit a highly crys-

talline perovskite structure, no formation of other phases was observed, except of gadolinium doped materials. The minority phase of cerium dioxide was identified in the case of gadolinium doped barium cerate. The experimental impedance spectra may be approximated using the equivalent circuit consisting of two or three serials R (resistor) and CPE (constant phase element) connected in parallel. Both bulk and grain boundary electrical conductivity were determined separately. The formation of acceptor centers in both cation sublattices of BaCeO<sub>3</sub> leads to considerable changes in the oxygen nonstoichiometry and electrical properties.

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